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WATER METALS NUMBER 6

R. J. Lishka, et al

Environmental Control Administration
Cincinnati, Ohio

1970

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WATER METALS NO. 6

REPORT NUMBER 37

Report of a Study Conducted by

ANALYTICAL REFERENCE SERVICE

R. J. Lishka and E. F. McFarren
Division of Criteria and Standards
Bureau of Water Hygiene

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service
Cincinnati, Ohio 45213
1970

FOREWORD

The Analytical Reference Service (ARS) is conducted by the Bureau of Water Hygiene of the Environmental Control Administration to evaluate laboratory methods in the environmental field. Cooperative studies by member organizations, who analyze identical samples and critically review methodology, provide the mechanism for:

> Evaluation of analytical procedures, including precision and accuracy, by comparison of the procedures and results reported by participating laboratories.
>
> Exchange of information regarding method characteristics.
>
> Improvement or replacement of existing methods by development of more accurate procedures, and development of new methodology for determination of new pollution compounds.

Samples are designed to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the membership, consultants, and the ARS staff. Notice of each study is sent to the entire membership. To those who desire to participate, a portion of the study sample is sent, along with data forms for reporting numerical values, a critique of the procedures used, comments on modifications, sources of error, difficulties encountered, or other pertinent factors. The results and comments received are compiled, and a report of each study is prepared.

Now primarily directed toward examination of water, in the past studies have included methods for analysis of air, milk, and food. Some studies are periodically repeated for the advantage of new members, the evaluation of new methods, or the reevaluation of existing methods.

The selection of studies is guided by requests from standard methods committees and the responses to questionnaires periodically circulated among the membership, which now includes 299 Federal, state, and municipal agencies; industries; universities; consulting firms; and foreign agencies.

COMPLETED STUDIES

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium; study No. 1 completed in 1956, No. 2 in 1958 and No. 3 in 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc; study No. 1 completed in 1957 and No. 2 in 1962. These same metals plus silver; study No. 3 completed in 1965. Except for the substitution of magnesium for aluminum, these same metals were analyzed by atomic absorption in 1967; study No. 4. Copper, manganese, and aluminum in the presence and absence of interferences; study No. 5 completed in 1969. Aluminum, beryllium and barium by atomic absorption; study No. 6 completed in 1970.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation by a specified procedure; study No. 1 completed in 1958 and No. 2 in 1961. Fluoride by ion-exchange and fluoride electrode; study No. 3 completed in 1969.
Water-Radioactivity	Gross beta activity; study No. 1 completed in 1959 and No. 2 in 1961. Gross beta and strontium-90 activity; study No. 3 completed in 1963.
Water-Surfactant	Surfactant in various waters; study No. 1 completed in 1959, No. 2 in 1963 and No. 3 in 1968.
Water-Oxygen Demand	Biochemical oxygen demand and chemical oxygen demand; study No. 1 completed in 1960. Chemical oxygen demand; study No. 2 completed in 1965.
Water-Trace Elements	Arsenic, boron, selenium, and beryllium; study No. 1 completed in 1962. These same metals plus vanadium; study No. 2 completed in 1966.

Freshwater Plankton	Evaluation of the precision and accuracy obtainable by the use of various methods of plankton counting and identification; study No. 1 completed in 1964.
Water-Nutrients	Silicate, phosphate, ammonia nitrogen, organic nitrogen, and nitrate nitrogen; study No. 1 completed in 1966. Ammonia nitrogen, nitrate nitrogen and ortho, poly, and organic phosphate; study No. 2 completed in 1969.
Water-Phenols	Phenol and 2,4-dichlorophenol in water by two specified methods; study No. 1 completed in 1966.
Water-Cyanides	Potassium cyanide and potassium ferricyanide in water by two specified methods; study No. 1 completed in 1967.
Water-Chlorine	Free and combined chlorine by nine different methods; study No. 1 completed in 1969.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass-fiber, high-volume filter mats; study No. 1 completed in 1958.
Air-Lead	Filter paper tape impregnated with lead; study No. 1 completed in 1961.
Air-Particulates	Microscopic identification of some common atmospheric particulates; study No. 1 completed in 1964.
Air-Sulfur Dioxide	Sulfur dioxide in air by a specified method; study No. 1 completed in 1963.
Water-Pesticides	Lindane, heptachlor epoxide, DDE, and dieldrin in water; study No. 1 completed in 1965. Lindane, heptachlor, aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, endrin, o,p'-DDT, p,p'-DDT, and methoxychlor in water; study No. 2 completed in 1968.

Food-Pesticides	DDT in milk; study No. 1 completed in 1962. Lindane, heptachlor epoxide, DDE, and dieldrin in milk; study No. 2 completed in 1965.

Copies of these reports are available from ARS on request as long as the present supply lasts. In most cases reports published prior to 1965 are no longer available. Order by title; namely, Water Metals No. 4, or Water Surfactant No. 3, etc.

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PREFACE

The present edition of Standard Methods for the Examination of Water and Wastewater does not contain a procedure for barium analysis; yet the drinking water standard for barium is set at 1.0 mg per liter. On the other hand there are several methods for aluminum in current use, but none are as precise or accurate as desirable. Since these metals as well as beryllium can be determined by atomic absorption spectrophotometry, using a nitrous oxide-acetylene burner, this study was proposed. Furthermore, this represents a logical extension of the method for the determination of the more common metals by atomic absorption spectrophotometry using an air-acetylene flame.

In a previous study (Water Metals No. 5) the ECR procedure for aluminum was evaluated and was found to be simpler than the aluminon procedure but not significantly better in precision or accuracy. In that study, however, none of the samples contained the lower concentrations of aluminum (0.02 to 0.03 mg per liter) where it is claimed that the method is more accurate and precise. Since one of the samples in this study was designed to contain these lower concentrations of aluminum, it seemed desirable also to request the participants to analyze these samples by the ECR method in order to collect data either to confirm or disprove this opinion.

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PARTICIPANTS IN THIS STUDY

Bio-Technics Laboratories, Inc., Los Angeles, California
Brown and Caldwell Laboratories, San Francisco, California
Calgon Corporation, Pittsburgh, Pennsylvania
City of Amarillo, Water Treatment Laboratory, Texas
City of Philadelphia Water Department, Pennsylvania
Connecticut State Department of Health, Hartford
Delaware Water and Air Resources Commission, Dover
Department of Energy, Mines and Resources, Ontario, Canada
DHEW, PHS, Water Supply and Sea Resources Program, Bethesda, Maryland
Department of Municipal Laboratories, Hamilton, Ontario, Canada
Department of Public Health, Edmonton, Alberta, Canada
Department of Public Health, Sydney N.S.W., Australia
Department of Water Resources, Durham, North Carolina
Division of Water Resources, Charleston, West Virginia
Emery Industries, Inc., Cincinnati, Ohio
First U.S. Army Medical Laboratory No. 1, Ft. George Meade, Maryland
Idaho Department of Health, Boise
Illinois State Water Survey, Peoria, Illinois
Lawrence Experiment Station, Massachusetts
Los Angeles Department of Public Works, Playa Del Rey, California
Louisiana State Department of Health, New Orleans
Mekoroth Water Company, Bnei-Brak, Israel
Ministere de la Sante du Quebec, Montreal, Canada
Minnesota Department of Health, Minneapolis
Monroe County Health Department Laboratory, Rochester, New York
Nassau County Department of Health, Hempstead, New York
New Jersey State Department of Health, Trenton
New Mexico Bureau of Mines, Socorro
New York State Department of Health, Albany
New York State Department of Health, Syracuse
North Carolina Department of Water and Air Resources, Raleigh
North Jersey District Water Supply Commission, Wanaque, New Jersey
Orange County Air Pollution Control District, Anaheim, California
Pan American World Airways, Patrick AFB, Florida
Pennsylvania Department of Health, Harrisburg
Perkin-Elmer Corporation, Norwalk, Connecticut
Philadelphia Suburban Water Company, Bryn Mawr, Pennsylvania
South African Council for Scientific and Industrial Research, Pretoria
Springwells Filtration Plant, Dearborn, Michigan
State Hygienic Laboratory, Des Moines, Iowa
State Water Survey Division, Urbana, Illinois
Trapelo/West, Div. L.F.E. Inc., Richmond, California
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United States Pipe and Foundry Company, Birmingham, Alabama
University of Leeds, England
USDI, FWPCA, Cincinnati, Ohio
USDI, FWPCA, Division of Research, Cincinnati, Ohio
USDI, FWPCA, Pomona, California
USDI, FWPCA, Wheeling Field Station, Wheeling, W. Va.
Utah State Division of Health, Salt Lake City

ABSTRACT

In this study, three samples were provided containing various concentrations of aluminum, beryllium, and barium at levels of interest in water supplies. Participants were provided with copies of an atomic absorption procedure for all three metals and the eriochrome cyanine R procedure for aluminum.

Both methods appear equally suitable for aluminum at concentrations greater than 0.3 mg/liter. At concentrations less than this the ECR procedure, although imprecise, would be preferred.

The atomic absorption technique appears suitable for the measurement of both beryllium and barium in water.

WATER METALS NO. 6

DESIGN OF THE STUDY

To evaluate the measurement of aluminum, beryllium, and barium by atomic absorption spectroscopy at concentrations of interest to water analysts, three samples were prepared containing these metals in different concentrations. To minimize adsorption, to obtain greater stability, and to reduce shipping costs, the samples were prepared as concentrated solutions and shipped in sealed, 25-ml glass ampoules.

The concentrations of aluminum, beryllium, and barium were such that when the participant diluted, as instructed, 5 ml of each concentrate with enough distilled water to make 1 liter, the samples would contain concentrations likely to be found in water supplies (see Table 1 for composition of samples).

Table 1. COMPOSITION OF SAMPLES

	mg/liter in diluted sample		
	Sample 1	Sample 2	Sample 3
Aluminum [$AlCl_3 \cdot 6H_2O$]	0.050	0.300	0.750
Beryllium [$Be(NO_3)_2 \cdot 3H_2O$]	0.005	0.050	0.100
Barium [$BaCl_2 \cdot 2H_2O$]	0.500	1.000	5.000

In analyzing the samples, the participants were requested to use the provided atomic absorption procedure for all three metals and, if desired, the provided eriochrome cyanine R (ECR) procedure for aluminum.

TREATMENT OF THE DATA

As the results of analysis were received from each participant, the data were reviewed, and, in the case of a suspected mathematical error, the reporting laboratory was asked to check the calculations and to submit a corrected value if an error was found.

The data were then coded and analyzed by computer for normality of distribution and subsequent rejection of outliers (see Appendix E) that were nonrepresentative because of errors in calculation, dilution, or other indeterminate factors.

The results for each sample were also plotted on normal probability paper as a visual check on normality of distribution and the possible presence of outliers. In a few cases it was found that the results submitted by certain laboratories exhibited a pronounced bias that was similar for each sample analyzed. Since it was obvious that a common factor such as incorrectly prepared samples, bad dilution water, or incorrectly standardized reference solutions was responsible, these values also were rejected. After rejection of outliers, the data were then statistically analyzed by computer for precision and accuracy (see Appendix D). Finally, the precision and accuracy of aluminum measurement by atomic absorption and by ECR were compared for significance of differences (see Appendix F).

Bar graphs are included in the text to provide a pictorial display of the data. Rejected values are indicated by broken bars, and values are given for bars off the scale of the chart.

Results were also submitted by participants who used methods differing from the two being studied. Unfortunately, not enough results for a specific procedure were submitted to permit statistical evaluation, but the results are shown in the tabulated data (see Appendix C) with method identity indicated by numbers corresponding to those in the bibliography of this report. In most cases, the method is merely a slight modification of the requested method.

RESULTS

Aluminum (Table 2; Figures 1-6)

The provided atomic absorption procedure was used by 18 participants, the ECR procedure by 35, and the aluminon procedure by 5. Although the latter data are shown in the summary tables for comparison, no firm conclusions can be made from so few results. The accuracy of all three methods, as indicated by their relative errors, was unsatisfactory for the 0.05 mg/liter concentration in sample 1. Much better accuracy, especially by atomic absorption, was obtained for samples 2 and 3, which contained 0.30 mg/liter and 0.75 mg/liter respectively.

For sample 1, the precision of the ECR procedure was significantly better than the atomic absorption and aluminon procedures although all three methods produced quite scattered results. For sample 2, the ECR results were significantly more precise than those obtained by atomic absorption, but there was no significant difference in precision for sample 3. As was the case for accuracy, much better precision was obtained for the higher concentrations in samples 2 and 3.

When both accuracy and precision are considered, the atomic absorption and ECR procedures appear equally satisfactory for aluminum concentrations of 0.30 mg/liter and higher but are unreliable for concentrations as low as 0.05 mg/liter. At such low concentrations, however, the ECR procedure would be the preferred method if measurement must be made.

Table 2. SUMMARY OF DATA ON ALUMINUM

Method	No. of results	No. of outliers	Mean	Mean error	Std. dev.	Rel. error	Rel. std. dev.
		Sample 1 (0.05 mg/liter)					
Atomic absorption	17	3	0.063	+0.013	0.048	26.0	76.2
ECR	35	3	0.039	-0.011	0.015	22.0	38.5
Aluminon	4	0	0.040	-0.010	0.043	20.0	107.5
		Sample 2 (0.30 mg/liter)					
Atomic absorption	18	3	0.302	+0.002	0.067	0.7	22.2
ECR	35	3	0.273	-0.027	0.045	9.0	16.5
Aluminon	4	0	0.268	-0.032	0.027	10.5	10.1
		Sample 3 (0.75 mg/liter)					
Atomic absorption	18	3	0.691	-0.059	0.114	7.9	16.5
ECR	34	3	0.679	-0.071	0.153	9.5	22.6
Aluminon	5	0	0.709	-0.041	0.212	5.5	30.0

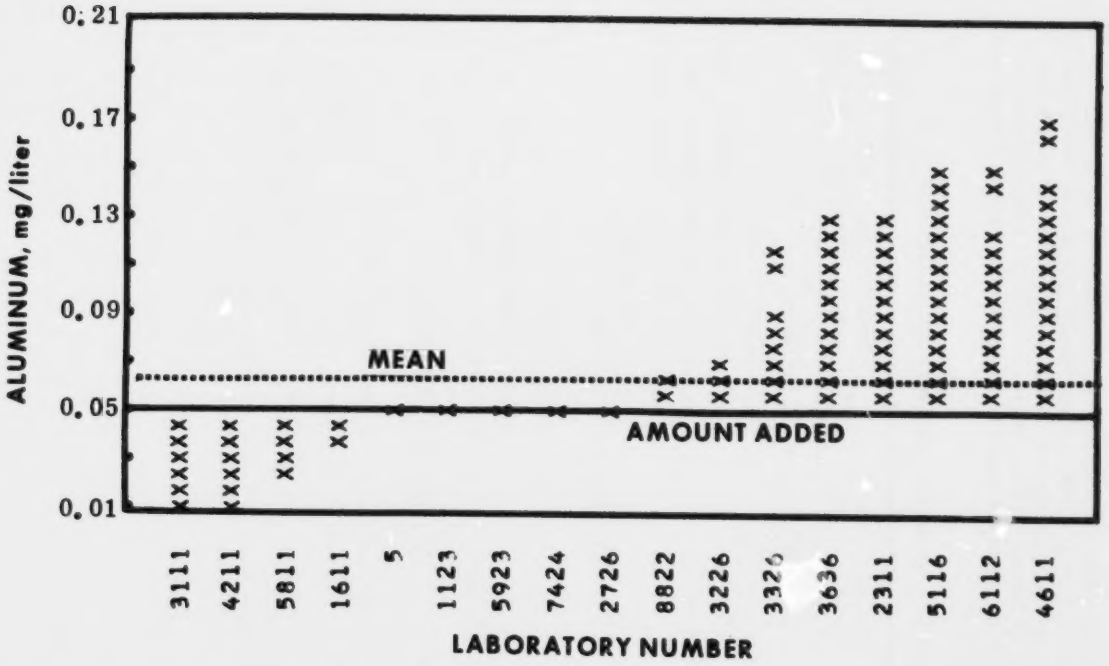

Figure 1. Bar graph for aluminum in sample 1 by atomic absorption.

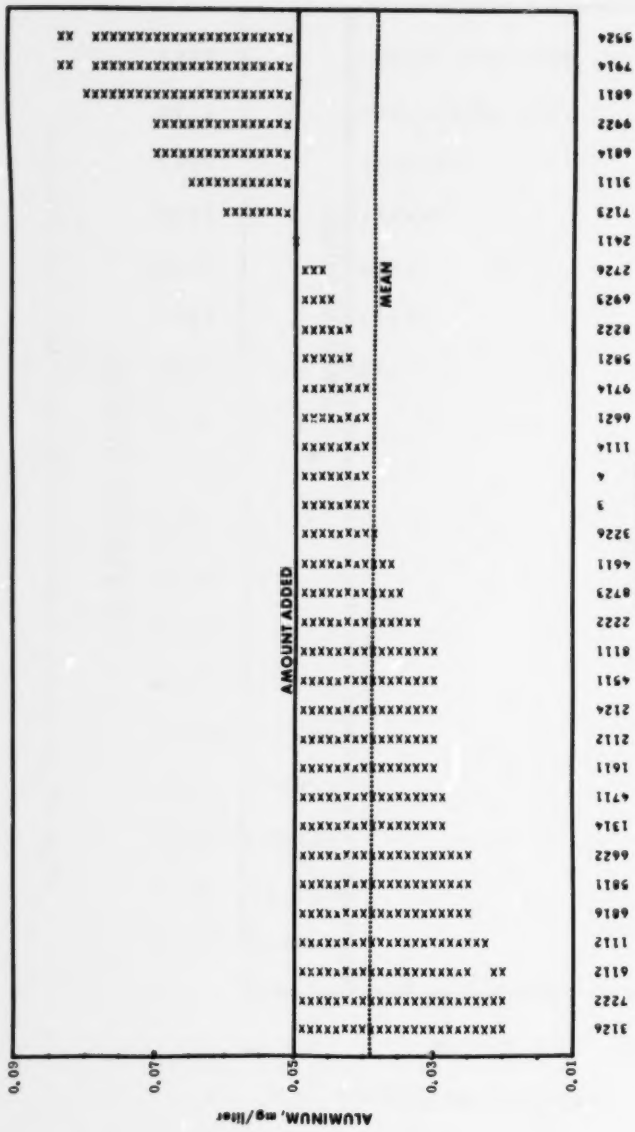

Figure 2. Bar graph for aluminum in sample i by ECR.

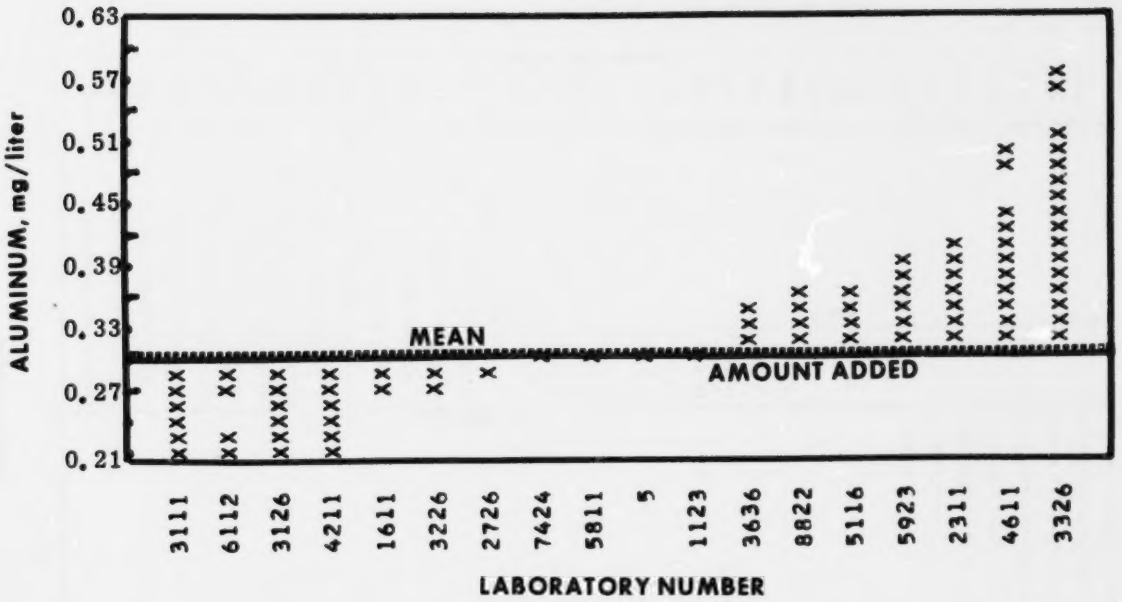

Figure 3. Bar graph for aluminum in sample 2 by atomic absorption.

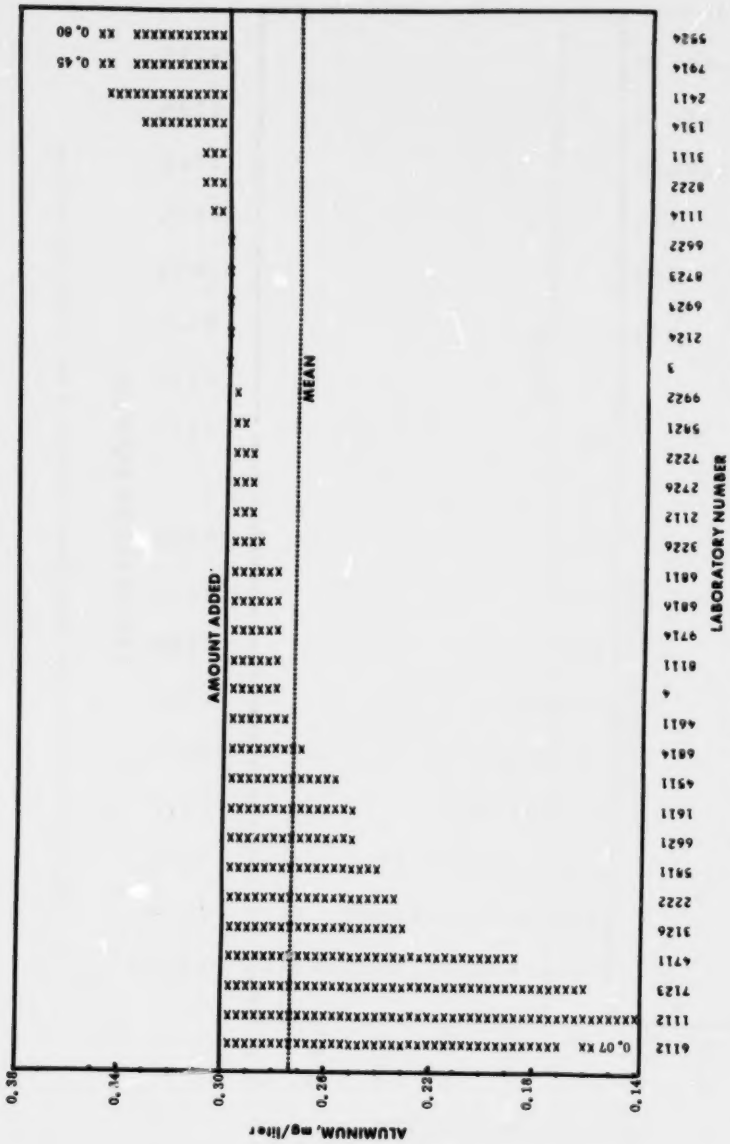

Figure 4. Bar graph for aluminum in sample 2 by ECR

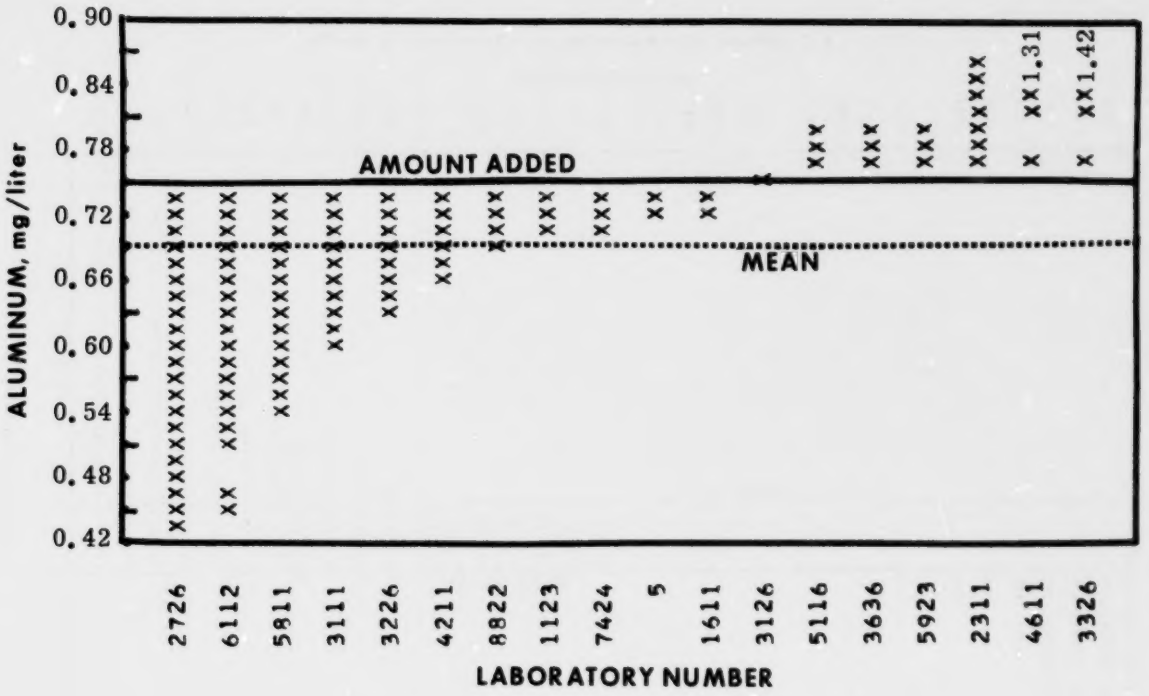

Figure 5. Bar graph for aluminum in sample 3 by atomic absorption.

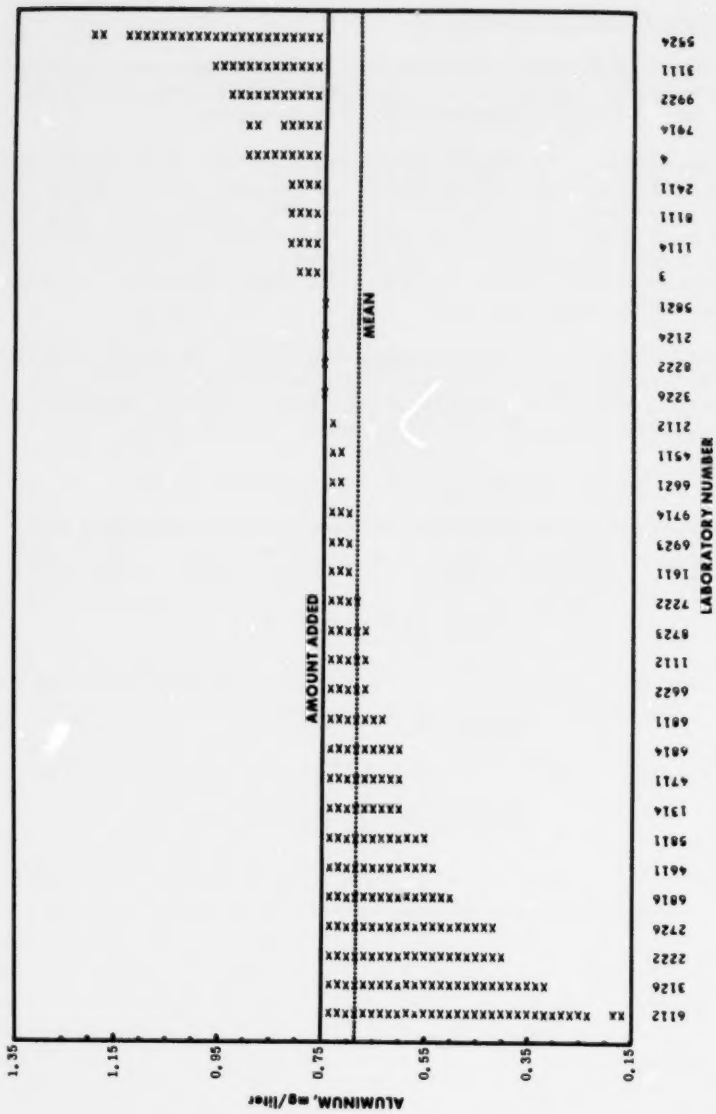

Figure 6. Bar graph for aluminum in sample 3 by ECR.

Beryllium (Table 3; Figures 7-9)

Eleven participants used the atomic absorption procedure for measuring beryllium, but the results submitted by two laboratories for all three samples were rejected because of gross errors.

The accuracy, as indicated by the relative error, is nearly the same for samples 2 and 3 but is much greater for sample 1. Although the relative error is much greater, the actual magnitude of the error, as indicated by the mean error, is the same as for sample 2 (0.001 mg/liter). Thus, it would appear that the concentration of sample 1 is approximately at the detection limit for the method, and a relative error of 20 percent at this level is really quite good.

As indicated by the relative standard deviation, the precision of the data is very similar for all three samples and leaves something to be desired. The relative simplicity of the method, however, and the excellent accuracy make it suitable for routine analysis of water.

Table 3. SUMMARY OF DATA ON BERYLLIUM

Method	No. of results	No. of outliers	Mean	Mean error	Std. dev.	Rel. error	Rel. std. dev.
		Sample 1 (0.005 mg/liter)					
Atomic absorption	10	1	0.006	+0.001	0.0017	20.0	34.0
		Sample 2 (0.050 mg/liter)					
Atomic absorption	11	2	0.051	+0.001	0.020	2.0	39.2
		Sample 3 (0.100 mg/liter)					
Atomic absorption	11	2	0.103	+0.003	0.036	3.0	35.0

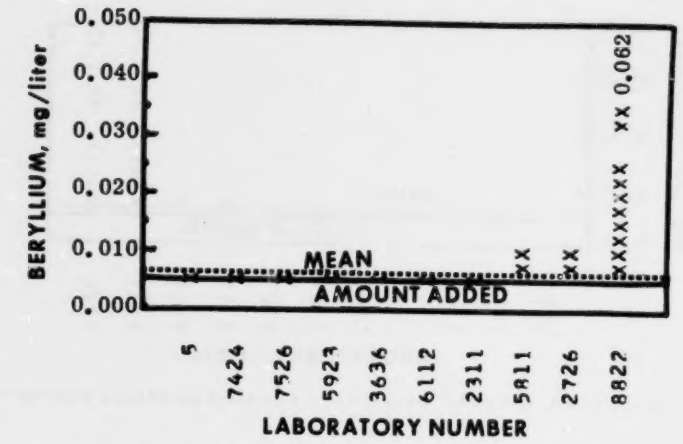

Figure 7. Bar graph for beryllium in sample 1 by atomic absorption.

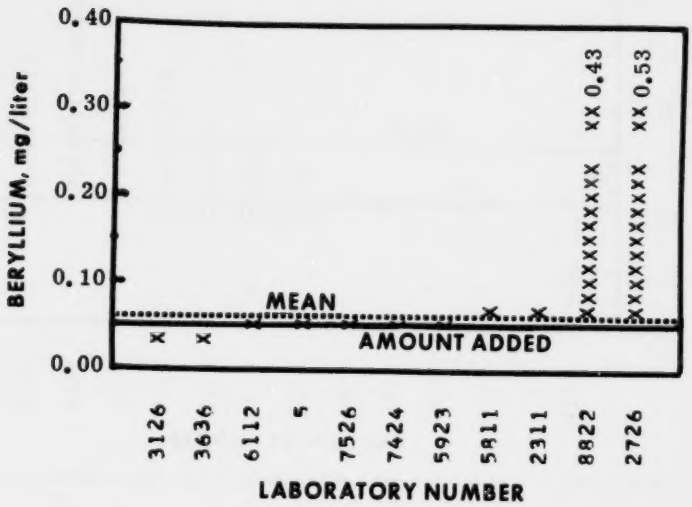

Figure 8. Bar graph for beryllium in sample 2 by atomic absorption.

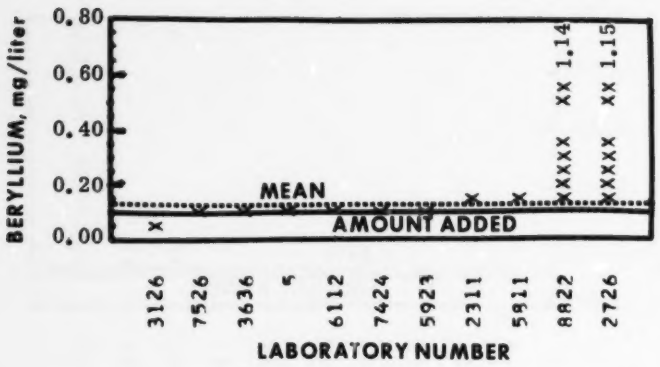

Figure 9. Bar graph for beryllium in sample 3 by atomic absorption.

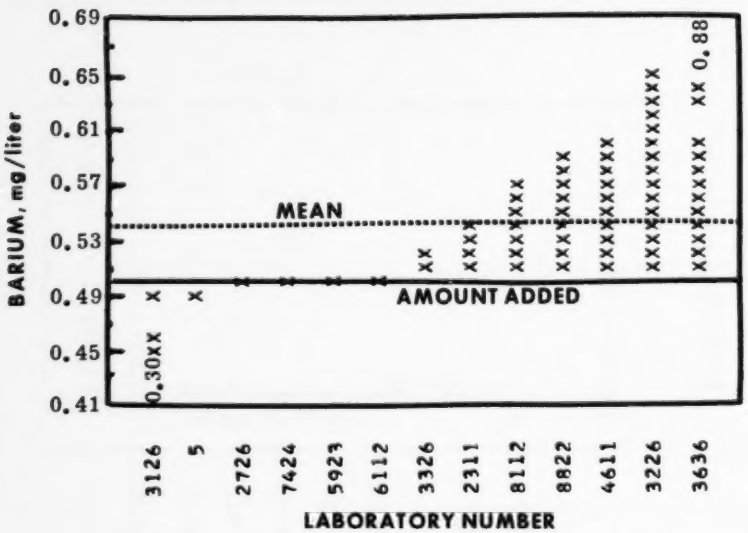

Figure 10. Bar graph for barium in sample 1 by atomic absorption.

Barium (Table 4; Figures 10-12)

Thirteen participants used the atomic absorption procedure for barium measurement. The results from one laboratory for all three samples were rejected, and the results from another laboratory for samples 1 and 2 were rejected.

Excellent accuracy and precision were obtained for all three samples although, as might be expected, they were least for sample 1 which contained only 0.50 mg/liter. Since the drinking water standard for barium is set at 1.0 mg/liter, the method appears satisfactory for water analysis. The relative standard deviation at this concentration is only 8.9 percent and the relative error only 2.7 percent.

The atomic absorption technique for barium measurement is not only very simple and rapid but is also the only reliable method available for routine water analysis. For higher concentrations, the colorimetric measurement of the chromate or the turbidimetric measurement of the sulfate have commonly been used.

Table 4. SUMMARY OF DATA ON BARIUM

Method	No. of results	No. of outliers	Mean	Mean error	Std. dev.	Rel. error	Rel. std. dev.
		Sample 1 (0.50 mg/liter)					
Atomic absorption	13	2	0.543	+0.043	0.054	8.6	10.0
		Sample 2 (1.00 mg/liter)					
Atomic absorption	13	2	1.027	+0.027	0.091	2.7	8.9
		Sample 3 (5.00 mg/liter)					
Atomic absorption	13	1	5.072	+0.072	0.188	1.4	3.7

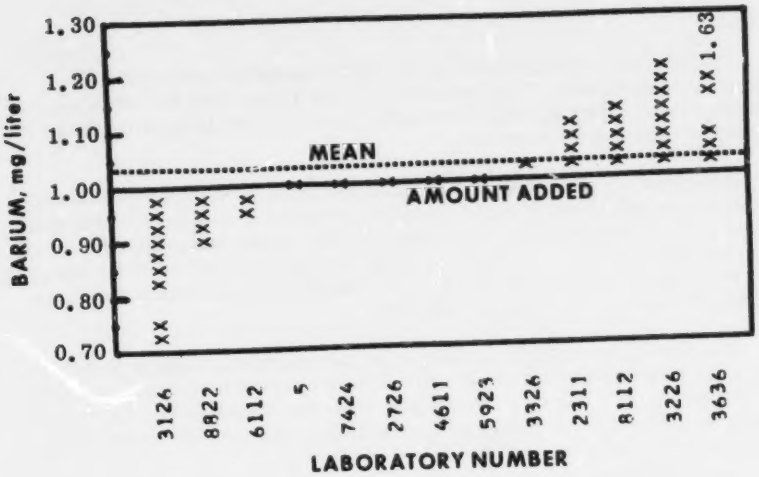

Figure 11. Bar graph for barium in sample 2 by atomic absorption.

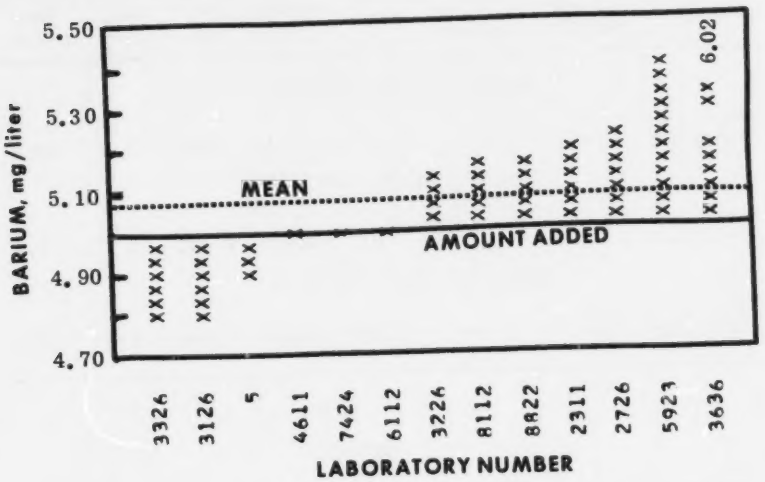

Figure 12. Bar graph for barium in sample 3 by atomic absorption.

COMMENTS OF THE PARTICIPANTS

Aluminum by ECR

1. "The method repeats very well at low concentrations. Wide variances occur at higher (above 0.300 mg/liter)."

2. "Reagent used was Alizarol Cyanine RC (Allied Chemicals). After phosphate removal, results were inconsistent. Submitted results were corrected for fluoride only."

3. "Standard curve skewed below 0.5 μg/50 ml."

4. "A fair amount of preliminary work was necessary before the samples were analyzed, since in calibration, values would occasionally show some divergence for no apparent reason, and low absorbance values were invariably obtained for 1 μg and 2 μg of aluminum. At a later stage, a new buffer solution was prepared and gave lower absorbance values with known amounts of aluminum. A third buffer solution gave results that agreed with neither of the other, and there was a tendency for orange colors to develop instead of red. The same reagents had been used to prepare all these buffers, and the pH values appeared to agree. There was an indication that the addition of EDTA did not complex all the aluminum in samples 2 and 3, though the proportion was quite small."

5. "No corrections made for fluoride or phosphate. The procedure is time-consuming."

6. "If samples are run by treating for phosphate interference the results are too high. It would appear that standards would have to be carried through the same procedure to correct for this."

7. "Sample 1 was very unsatisfactory."

8. "Color constantly fades-not very stable."

9. "Poor precision, especially at low concentrations. Procedure could stand simplification."

10. "Difficulty in obtaining precise calibration curve."

Aluminum by Atomic Absorption

1. "Sample #1 using 200-ml sample and a scale setting of 5 only gave a reading of 0.8 which I consider too low for accuracy."

2. "10 x scale expansion used; much noise. Clogging of burner occurred."

3. "Our water cooled burner head "carboned up" rapidly causing an ever-changing base line and making readings difficult to obtain."

4. "Could not attain anything like sufficient sensitivity by aspirating chloroform. Complex was transferred to a slightly acid aqueous solution which then gave proper sensitivity. Absorbance curve was not linear. High standard response was low."

5. "There is a typographical error (section 3.6 of procedure) in the formula for potassium aluminum sulfate. It should be $K_2Al_2(SO_4)_4 \cdot 24\ H_2O$ or $KAl(SO_4)_2 \cdot 12H_2O$, but not $K_2Al_2(SO_4)_2 \cdot 24\ H_2O$."

6. "Worked well."

7. "Sample 1 is barely detectable."

Beryllium by Atomic Absorption

1. "10 x scale expansion used; much noise. Clogging of burner occurred."

2. "The direct method performed better, down to 0.01 mg/liter Be, than did the extraction procedure."

Barium by Atomic Absorption

1. "At high gas flow rates, flame gave emissive response for Ba standards. At lower flow rates, response was much too low. Could not improve situation by varying gas mixture."

2. "Extremely unstable with N_2O flame, therefore acetylene-air flame used with Boling (3-slot) burner."

3. "A less sensitive line was used (555.8 mμ - sensitivity 2.4 μg/ml for 1% absorption) due to excessive and uncorrectable noise at the suggested wave length."

4. "Method seemed to perform well."

SUMMARY AND CONCLUSIONS

In this study, the participants were requested to use the provided atomic absorption procedures for the analysis of aluminum, beryllium,

and barium in three samples of various concentrations. Also provided was the colorimetric eriochrome cyanine R procedure for aluminum.

The two methods for aluminum appear equally suitable for concentrations of 0.3 mg/liter or greater. At concentrations less than this both methods become imprecise, but the ECR procedure would be the preferred method. The chief complaint about the ECR method was lack of precision. The atomic absorption procedure suffered from low sensitivity and high background noise. It is likely that improved source lamps will increase the sensitivity and reduce noise.

The measurement of beryllium by atomic absorption appears sufficiently accurate and precise for water analysis, when the low concentrations being measured are considered. High background noise was encountered at high scale expansion.

The best accuracy and precision were obtained for the measurement of barium by atomic absorption. Undoubtedly contributing to the excellence of the results are the fact that barium was present in higher concentrations than the other metals and the much greater simplicity of the technique, which involved only the addition of sodium chloride to the sample before aspiration. The measurement of aluminum and beryllium required the more complex procedure of chelation with pH adjustment followed by serial extraction and aspiration of the organic phase.

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2. ECR method provided - Appendix B.

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4. Atomic absorption - aqueous after concentrating (no reference).

5. Atomic absorption - air and acetylene flame (no reference).

6. Atomic absorption - methyl iso-butyl ketone extraction (no reference).

7. Emission spectroscopy (no reference).

8. Ferron - orthophenanthroline method - Rainwater, F. and L. L. Thatcher. Methods for Collection and Analysis of Water Samples. Geological Survey Water-Supply Paper 1454. 1960.

B. Beryllium

1. Atomic absorption method provided - Appendix A.

2. Atomic absorption - direct aqueous (no reference).

3. Improvements in the Fluorometric Determination of Submicrogram Quantities of Beryllium. Sill, C. W., C. P. Willis, and J. K. Flygare. Anal. Chem. 33:1671, 1961.

4. Photometric Determination of Beryllium. Hill, U. T. Anal. Chem. 30:521, 1958.

5. Emission spectroscopy (no reference).

C. Barium

1. Atomic absorption method provided - Appendix A.

2. Atomic absorption - air and acetylene flame (no reference).

3. Atomic absorption - different wavelength - 555.8 mμ (no reference).

4. Rhodizonic acid (no reference).

5. Emission spectroscopy (no reference).

6. Flame emission of EDTA complex (unpublished).

7. Turbidimetric (no reference).

APPENDICES

APPENDIX A

METALS IN NATURAL AND TREATED WATERS IN THE ABSENCE OF GROSS POLLUTION BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Most metals can be determined by atomic absorption with an air-acetylene flame (see JAWWA. 60:739, 1968). A few, however, require a higher temperature flame to dissociate the molecules. Metals that can be determined by use of the higher temperature nitrous oxide-acetylene burner include aluminum, beryllium, and barium. Whereas barium can be determined by aspiration of the aqueous solution directly into the flame, the method is not sensitive enough to determine aluminum and beryllium at the concentrations of interest to water plant operators, unless these two metals are concentrated by complexing with a chelating compound and extracting into an organic solvent.

1. GENERAL DISCUSSION

1.1. Principle: Atomic absorption resembles emission flame photometry in that a sample is aspirated into a flame and atomized. The major difference rests in the fact that flame photometry measures the amount of light emitted, whereas in atomic absorption spectroscopy a light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption is more sensitive because it depends upon the presence of free, unexcited atoms and in the usual flames the ratio of unexcited to excited atoms at a given moment is very high. Since each metallic element has its own characteristic absorption wavelength, a source lamp composed of that element is employed for each element, and hence the method is relatively free of spectral or radiation interferences. The amount absorbed in the flame is proportional to the concentration of the element in the sample.

1.2. Interference: The most troublesome type of interference is usually termed "chemical" and results from the lack of absorption from atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. Barium fits into the former and aluminum and beryllium into the latter category, and as a result, the nitrous oxide-acetylene flame is recommended because of its higher temperature. In addition, barium may undergo ionization in the flame, and the ground state (potentially absorbing) population is thereby reduced. This situation can be overcome by the addition of an excess of a cation having a similar or lower ionization potential.

2. APPARATUS

2.1. Atomic absorption spectrophotometer.

2.2. Burner: Nitrous oxide burner head with 2-inch slot (reduces overheating frequently encountered with 3-inch slot). When using a nitrous oxide acetylene flame always remember to clean the burner slot frequently by using a razor blade or equivalent prior to ignition to dislodge the carbon crust that forms along the slit surface approximately every 20 minutes.

2.3. Separatory funnels, 250 ml, preferably with teflon stopcocks, for extractions with organic solvents.

2.4. Glassware: All glassware, including sample bottles, should be rinsed with 1 + 1 HNO_3 followed by deionized distilled water to avoid contamination errors.

3. REAGENTS

3.1. Deionized distilled water: Prepare by passing distilled water through a mixed bed of ion-exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

3.2. Nitric acid, conc.

3.3. Sodium chloride solution: Dissolve 250 grams of reagent-grade sodium chloride in distilled water and make up to 1,000 ml.

3.4. Stock barium solution: Dissolve 1.7787 grams barium chloride ($BaCl_2 \cdot 2H_2O$) in 1,000 ml distilled water to obtain a solution containing 1.0 mg/ml barium.

3.5. Stock beryllium solution: Dissolve 20.7574 grams of beryllium nitrate, $Be(NO_3)_2 \cdot 3H_2O$, in 1,000 ml distilled water to obtain a solution containing 1.0 mg/ml beryllium.

3.6. Stock aluminum solution: Dissolve 8.792 grams of potassium aluminum sulfate $K_2Al_2(SO_4)_4 \cdot 24\ H_2O$ in distilled water and dilute to 1 liter in a volumetric flask to obtain a solution containing 0.5 mg/ml of aluminum.

3.7. Standard solutions: In general, prepare a series of standard solutions containing 0.005 to 1.0 mg/liter metal by appropriate dilution of the stock solution.

3.8. Fuel and oxidant: Use nitrous oxide-acetylene flame for all the metals in Table A-1.

3.9. Special reagents for determining low concentrations of aluminum and beryllium:

a. 8-hydroxy-quinoline: Dissolve 20 grams in 1 N acetic acid (60 ml glacial acetic acid per liter) and make up to a volume of 1 liter with the 1 N acid.

b. Buffer: Dissolve 200 grams of ammonium acetate and 70 ml of concentrated ammonium hydroxide in distilled water and make up to a total volume of 1 liter.

c. Chloroform.

4. PROCEDURE

4.1. Pretreatment of sample: Acidify all water samples with nitric acid (1 ml concentrated nitric acid per 100 ml sample) and autoclave at 250° F for 1 hour to solubilize particulate matter, and readjust volume, if necessary.

4.2. Precaution: Install the spectrophotometer on a level bench or table with the burner under a vent.

Table A-1. Wavelength Settings and Sensitivity of Metal Determinations

Metal	Wavelength, mμ	Sensitivity, mg/liter per 1%[a]
Aluminum	309.3	1.0[b]
Barium	553.6	0.2
Beryllium	234.8	0.1[c]

[a] mg/liter metal for 1% absorption in an aqueous solution.

[b] 0.05 if extracted.

[c] 0.005 if extracted.

4.3. Instrument operation: Because the differences between the makes and models of satisfactory atomic absorption spectrophotometers render impossible the formulation of detailed instructions applicable to every instrument, follow the manufacturer's operating instructions. As a rule, choose the correct hollow cathode lamp, install and align in the instrument; position the monochromator at the correct wavelength (Table A-1); select the proper monochromator slit width; set the light source

current according to the manufacturer's recommendation; light the flame and regulate the flow of fuel and oxidant; adjust the burner for maximum percent absorption and stability; and balance the photometer. Then run the standards that are needed for the working curves and plot the concentrations of the standards against absorbance. If necessary on some instruments, convert percent absorption to absorbance. (The calibration curves are nearly linear for most elements.) Next run the samples and read the concentration of each sample from the calibration curve. For best results run standards each time a sample or series of samples are run.

4.4. Special procedure for barium: To overcome ionization interference in the flame, add 2 ml sodium chloride solution to 100 ml sample before aspiration. Prepare standards similarly to contain 2,000 mg/liter sodium.

4.5. Special procedural steps for low concentrations of aluminum and beryllium: To 100 ml of sample add 2 ml of 8-hydroxy quinoline solution and 3 ml of buffer solution. Adjust the mixture, if necessary, to a pH of 8.0 ± 0.5 and then extract with 5 ml of chloroform. Repeat the extraction with a second 5 ml of chloroform and combine the two extracts. Determine the amount of metal in the organic phase by comparison with standards that have been similarly extracted.

4.6. Aspiration of an organic solvent into the flame: When working with organic solvents, reduce the fuel-to-air ratio because the burning of the organic solvent contributes to the fuel supply and in addition to lifting the flame off the burner may produce an undesirable luminescent flame. In setting the fuel-to-air ratio of the gas mixture at the burner, start with the settings recommended by the manufacturer for the analysis and gradually reduce the fuel flow (while the solvent is being aspirated) until the flame is similar to the flame before aspiration of the organic solvent. With the nitrous oxide burner, approximately double the flow of acetylene is required over that normally used for the air-acetylene burner, and the acetylene should be adjusted until the flame is a rose-red.

5. CALCULATION

5.1. For aqueous sample refer directly to the calibration curve

$$\text{mg/liter metal} = (\text{mg/liter in aliquot}) \times D$$

where $D = \text{dilution ratio} = \dfrac{\text{ml sample} + \text{ml water} + 1\ (\text{ml acid})}{\text{ml sample}}$

5.2. For extracted sample refer to the extracted standard calibration curve.

mg/liter metal = (mg/liter in aliquot)

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1. Atomic Absorption Methods Manual, Volume I. Jarrell-Ash Company, Waltham, Massachusetts, 1966.

2. Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corporation, Norwalk, Connecticut. 1964 with supplement of 1966.

3. Goon, E., Petley, J.E., McMullen, W.H., and Wiberly, S.E., Fluorometric Determination of Aluminum by Use of 8-Quinolinol. Anal. Chem. 25:608 (1953).

APPENDIX B

ERIOCHROME CYANINE R METHOD FOR ALUMINUM

Aluminum is the third most abundant element of the earth's crust, occurring in minerals, rocks, and clays. This wide distribution accounts for the presence of aluminum in practically all natural water supplies, as a soluble salt, colloid, or insoluble compound. Soluble, colloidal, and insoluble aluminum may appear additionally in treated water as a residual from alum coagulation. There are many conflicting statements in the literature about the amount of this residual, but recent work[1] indicates that filtered water from a modern rapid sand filtration plant should have an aluminum concentration between 0.02 and 0.05 mg/liter.

1. GENERAL DISCUSSION

1.1. Principle: Dilute aluminum solutions buffered to a pH of 6.0 produce with Eriochrome Cyanine R dye a red to pink complex that exhibits maximum absorption at 535 mμ. The intensity of the developed color is influenced by the aluminum concentration, reaction time, temperature, pH, alkalinity, and the concentration of other accompanying ions in the sample. To compensate for color and turbidity, the aluminum in one portion of sample is complexed with EDTA to provide a blank. The interference of iron and manganese, two elements often found in water, is eliminated by the addition of ascorbic acid. The optimum aluminum range lies between 0.02 and 0.35 mg/liter but can be extended upward by sample dilution.

1.2. Interference: Negative errors are caused by both fluorides and polyphosphates. When the fluoride concentration is constant, the percentage of error decreases with increasing amounts of aluminum. Since the fluoride concentration is often known, or can readily be determined, fairly accurate results can be obtained by adding the known amount of fluoride to a set of standards. If less accuracy can be tolerated, a simpler correction can be determined from the family of curves in Figure B-1. A procedure is given for the removal of complex phosphate interference. Orthophosphates in concentrations of less than 10 mg/liter do not interfere. The interference caused by even small amounts of alkalinity is removed by acidifying the sample just beyond the neutralization point of methyl orange. Sulfates do not interfere up to a concentration of 2,000 mg/liter.

1.3. Minimum detectable concentration: The minimum aluminum concentration detectable by this method in the absence of fluorides and complex phosphates is approximately 6 μg/liter.

1.4. Sample handling: Samples should be collected in clean, acid-rinsed bottles and should be examined as soon as possible after collection.

If the concentration of soluble aluminum only is desired, a portion of the sample should be filtered through a 0.45-μ membrane filter and the filtrate used for the determination. Filter paper, absorbent cotton, and glass wool are completely unsuited for filtering any solution that is to be tested for aluminum, since they will remove most of the soluble aluminum.

2. APPARATUS

2.1. Colorimetric equipment: One of the following is required:

a. Spectrophotometer, for use at 535 mμ and utilizing a light path of 1 cm or longer.

b. Filter photometer, providing a light path of 1 cm or longer and equipped with a green filter showing maximum transmittance between 525 and 535 mμ.

c. Nessler tubes, 50 ml, tall form, matched.

2.2. Glassware: All glassware must be treated with warm 1 + 1 HCl and then rinsed with aluminum-free distilled water to avoid errors due to materials adsorbed on the glass. Rinse sufficiently to remove all acid.

3. REAGENTS

Use reagents low in aluminum, and aluminum-free distilled water.

3.1. Stock aluminum solution: The metal (a) or the salt (b) may be used for the preparation of the stock solution, which contains 0.500 mg Al per 1.00 ml.

a. Dissolve 0.5000 g ACS-grade aluminum metal in 10 ml of conc. HCl by heating gently. Dilute to 1 liter in a volumetric flask with distilled water.

b. Dissolve 8.792 g potassium aluminum sulfate (also called potassium alum), $K_2Al_2(SO_4)_4 \cdot 24\ H_2O$, in distilled water and dilute to 1 liter in a volumetric flask.

3.2. Standard aluminum solution: Dilute 10.00 ml of the stock aluminum solution to 1 liter in a volumetric flask with distilled water; 1.00 ml = 5 μg Al. Prepare daily.

3.3. Sulfuric acid, 0.02 N and 6 N.

3.4. Ascorbic acid solution: Dissolve 0.1 g ascorbic acid in distilled water and make up to 100 ml in a volumetric flask. Prepare fresh daily.

3.5. Buffer solution: Dissolve 136 g sodium acetate, $CHCOONa \cdot 3H_2O$, in water, add 40 ml 1-N acetic acid, and dilute to 1 liter.

3.6. Stock dye solution: A number of products are available. Any of the following may be used:

a. Solochrome cyanine R-200[2] or eriochrome cyanine[3]: Dissolve 100 mg of the dye in distilled water and dilute to 100 ml in a volumetric flask. This solution should have a pH value of about 2.9.

b. Eriochrome cyanine R[4]: Dissolve 300 mg of the dye in about 50 ml distilled water. Adjust the pH value, which will be about 9, to about 2.9 with 1+ 1 acetic acid. (Approximately 3 ml will be required.) Dilute with distilled water to 100 ml.

c. Eriochrome cyanine R[5]: Dissolve 150 mg of the dye in about 50 ml distilled water. Adjust the pH value, which will be about 9, to about 2.9 with 1 + 1 acetic acid. (Approximately 2 ml will be required.) Dilute with distilled water to 100 ml.

Stock solutions, prepared as described above, have excellent stability. They can be kept for at least a year, and perhaps longer.

3.7. Working dye solution: Dilute 10.0 ml of any one of the stock dye solutions to 100 ml in a volumetric flask with distilled water. Working solutions are stable for at least 6 months.

3.8. Methyl orange indicator solution.

3.9. 0.01 M EDTA (di-sodium ethylene-diamine tetra acetate): Weigh 3.7 g of the reagent, dissolve in distilled water, and dilute to 1 liter.

3.10. Sodium hydroxide, 1 N and 0.1 N.

4. PROCEDURE

Preparation of calibration curve:

4.1. Prepare a series of aluminum standards from 0 to 7 μg (0 to 280 μg/liter based on a 25-ml sample) by accurately measuring the calculated volumes of standard aluminum solution into 50-ml volumetric flasks or nessler tubes. Add distilled water to a total volume of approximately 25 ml.

4.2. Add 1 ml 0.02 N sulfuric acid to each standard and mix. Follow with 1 ml ascorbic acid solution and mix.

4.3. Add 10 ml buffer solution and mix.

4.4. Using a volumetric pipette, add 5 ml of working dye reagent and mix. Immediately make up to a volume of 50 ml with distilled water. Mix and let stand for 5 to 15 min. (The color begins to fade after 15 min.)

4.5. Read the transmittance or absorbance on a spectrophotometer using a wavelength of 535 mμ or a green filter providing maximum transmittance between 525 and 535 mμ. Adjust the instrument to 100 percent transmittance or zero absorbance with the standard containing no aluminum.

4.6. Plot a calibration curve relating micrograms aluminum to the instrument reading.

Sample treatment in the absence of fluoride and complex phosphates:

4.7. Place a 25.0-ml sample, or an aliquot diluted to 25 ml, in a porcelain dish or flask, add a few drops of methyl orange indicator, and titrate with 0.02 N sulfuric acid to a faint pink color. Record reading and discard this sample.

4.8. To two similar samples, at room temperature, add the same amount of 0.02 N acid used in the titration and 1 ml in excess.

4.9. To one of the samples add 1 ml EDTA solution. This one will serve as a blank by complexing any aluminum present and compensating for color and turbidity.

4.10. Add 1 ml ascorbic acid to the blank and sample, and continue to follow the procedure from 4.3 through 4.4.

4.11. Set the instrument to zero absorbance or 100 percent transmittance using the EDTA blank. Read the transmittance or absorbance of the sample and determine the aluminum concentration from the previously prepared calibration curve.

4.12. If photometric equipment is not available, prepare and treat the standards and a sample, as described above, in 50-ml nessler tubes. Make up to the mark with distilled water and compare the color of the sample with the standards after a 5 to 15 min. contact time. A sample treated with EDTA is not needed when nessler tubes are used. If the sample contains turbidity or color, the use of nessler tubes may result in considerable error.

4.13. Removal of phosphate interference: Add 1.7 ml 6 N sulfuric acid to 100 ml of sample in a 200-ml Erlenmeyer flask.

4.14. Heat on a hot plate for at least 90 min., keeping the solution temperature just below the boiling point.

4.15. At the end of the heating period, the solution volume should be about 25 ml. Add distilled water whenever necessary to keep it at or above that volume.

4.16. After cooling, neutralize the solution to a pH value between 4.3 and 4.5 with sodium hydroxide, using 1 N hydroxide at the start and 0.1 N for the final fine adjustment, and a pH meter.

4.17. Make up to 100 ml with distilled water, mix, and use a 25 ml aliquot for the aluminum test.

4.18. Run a blank in the same manner using 100 ml of distilled water and 1.7 ml 6 N sulfuric acid, and subtract it from the sample or use it to set the instrument to zero absorbance or 100 percent transmittance before reading the sample.

Sample treatment in the presence of fluoride:

4.19. Measure the fluoride concentration of the sample by the SPADNS method or electrode method, using sufficient citrate solution to complex the aluminum.

4.20. Perform one of the following:

a. Add the same amount of fluoride as in the sample to each aluminum standard.

b. Determine the fluoride correction from the set of curves in Figure B-1. This method may be used when a slight loss in accuracy can be tolerated.

5. CALCULATION

$$\text{mg/liter Al} = \frac{\mu\text{g Al}}{\text{ml sample}}$$

REFERENCES

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3. A product of K & K Labs., Plainview, N. Y.

4. A product of Pfaltz and Bauer, Inc., Flushing, N. Y.

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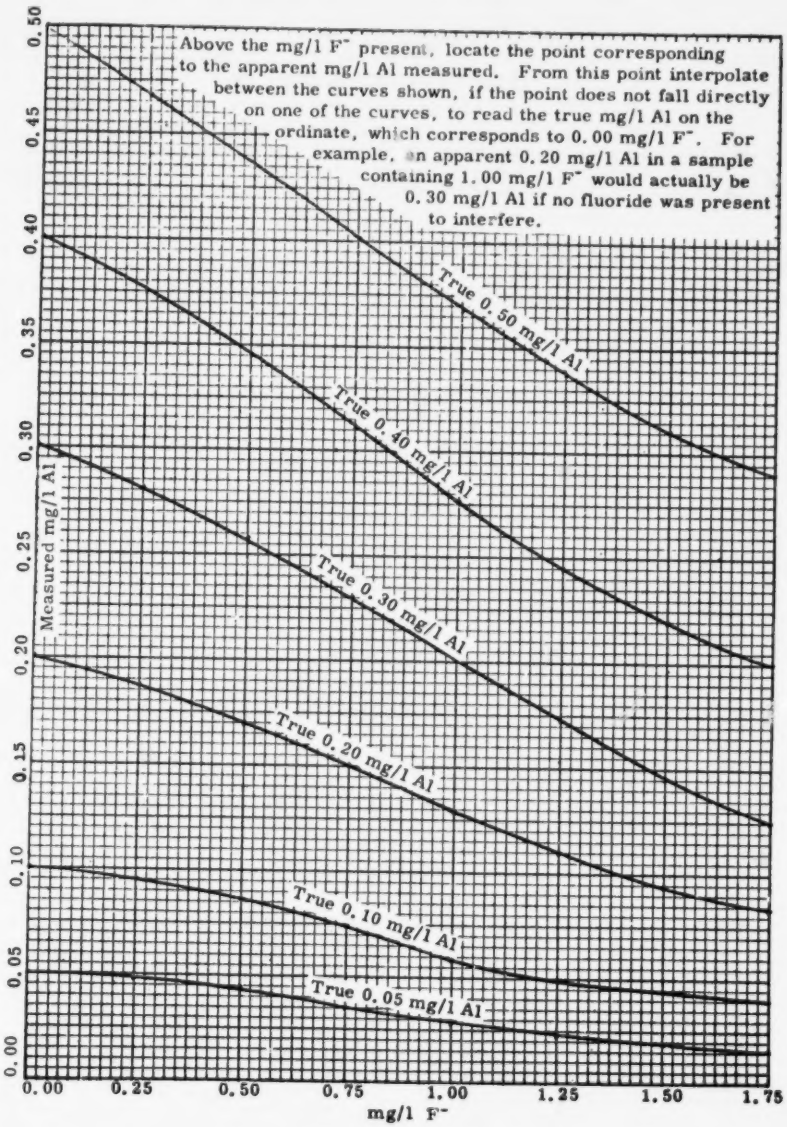
Above the mg/l F⁻ present, locate the point corresponding to the apparent mg/l Al measured. From this point interpolate between the curves shown, if the point does not fall directly on one of the curves, to read the true mg/l Al on the ordinate, which corresponds to 0.00 mg/l F⁻. For example, an apparent 0.20 mg/l Al in a sample containing 1.00 mg/l F⁻ would actually be 0.30 mg/l Al if no fluoride was present to interfere.
True 0.50 mg/l Al
True 0.40 mg/l Al
True 0.30 mg/l Al
True 0.20 mg/l Al
True 0.10 mg/l Al
True 0.05 mg/l Al
Measured mg/l Al
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.00
0.25
0.50
0.75
1.00
1.25
1.50
1.75
mg/l F⁻

Figure B-1. True mg/liter Aluminum Curves

APPENDIX C

TABULATION OF RESULTS

Table C-1. Sample 1: Aluminum (0.05 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3	0.04	2	3611	0.05	4
4	0.04	2	3636	0.13	1
5	0.05	1	4211	0.01	1
1112	0.02	2	4511	0.03	2
1114	0.04	2	4611	0.17	1
1123	0.05	1	4611	0.04	2
1314	0.03	2	4711	0.03	2
1611	0.03	2	5116	0.15	1
1611	0.04	1	5524	0.08	2
2112	0.03	2	5811	0.03	2
2124	0.03	2	5811	0.02	1
2222	0.03	2	5821	0.04	2
2311	0.13	1	5923	0.05	1
2411	0.05	2	6112	0.02	2
2726	0.05	2	6112	0.15	1
2726	0.06	1	6112	0.02	3
3111	0.01	1	6621	0.04	2
3111	0.07	2	6622	0.03	2
3126	0.02	2	6811	0.08	2
3226	0.07	1	6814	0.07	2
3226	0.04	2	6816	0.03	2
3226	0.02	6	6923	0.05	2
3326	0.10	3	7123	0.06	2
3326	0.12	1	7222	0.02	2

(Table C-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7424	0.05	1	8222	0.04	2
7424	0.05	8	8723	0.03	2
7914	0.08	2	8822	0.07	1
8111	0.03	2	9714	0.00	3
8111	0.04	3	9714	0.04	2
8112	0.05	4	9922	0.07	2

Table C-2. Sample 2: Aluminum (0.30 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3	0.30	2	3326	0.57	1
4	0.28	2	3326	0.52	3
5	0.31	1	3611	0.16	4
1112	0.14	2	3636	0.35	1
1113	0.68	7	4211	0.21	1
1114	0.31	2	4511	0.26	2
1123	0.31	1	4611	0.50	1
1314	0.34	2	4611	0.27	2
1611	0.25	2	4711	0.19	2
1611	0.26	1	5116	0.37	1
2112	0.29	2	5524	0.60	2
2124	0.30	2	5811	0.30	1
2222	0.23	2	5811	0.24	2
2311	0.42	1	5821	0.29	2
2411	0.35	2	5923	0.40	1
2726	0.28	1	6112	0.07	2
2726	0.29	2	6112	0.23	3
3111	0.31	2	6112	0.20	1
3111	0.20	1	6621	0.25	2
3126	0.21	1	6622	0.30	2
3126	0.23	2	6622	0.27	3
3226	0.29	2	6811	0.28	2
3226	0.27	6	6814	0.27	2
3226	0.27	1	6816	0.28	2

(Table C-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6923	0.30	2	8112	0.26	4
7123	0.16	2	8222	0.31	2
7222	0.29	2	8723	0.30	2
7424	0.30	1	8822	0.36	1
7424	0.30	8	9714	0.28	3
7914	0.45	2	9714	0.28	2
8111	0.29	3	9922	0.29	2
8111	0.28	2			

Table C-3. Sample 3: Aluminum (0.75 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
3	0.80	2	3326	1.42	1
4	0.90	2	3326	1.01	3
5	0.71	1	3611	0.72	4
1112	0.66	2	3636	0.80	1
1113	1.65	7	4211	0.65	1
1114	0.82	2	4511	0.71	2
1123	0.70	1	4611	1.31	1
1314	0.59	2	4611	0.52	2
1611	0.72	1	4711	0.60	2
1611	0.70	2	5116	0.80	1
2112	0.72	2	5524	1.20	2
2124	0.76	2	5811	0.53	1
2222	0.39	2	5811	0.55	2
2311	0.87	1	5821	0.76	2
2411	0.83	2	5923	0.80	1
2726	0.43	1	5923	0.80	4
2726	0.41	2	6112	0.42	3
3111	0.98	2	6112	0.45	1
3111	0.59	1	6112	0.16	2
3126	0.31	2	6621	0.70	2
3126	0.75	1	6622	0.65	3
3226	0.74	2	6622	0.65	2
3226	0.76	6	6811	0.63	2
3226	0.63	1	6814	0.60	2

(Table C-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
6816	0.50	2	8112	0.67	4
6923	0.70	2	8222	0.75	2
7222	0.67	2	8723	0.66	2
7424	0.70	1	8822	0.69	1
7424	0.75	8	9714	0.70	2
7914	0.90	2	9714	0.70	3
8111	0.82	2	9922	0.94	2
8111	0.76	3			

Table C-4. Sample 1: Beryllium (0.005 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5	0.005	1	5923	0.005	1
1113	0.010	5	6112	0.006	1
2311	0.007	1	7424	0.005	1
2726	0.011	1	7526	0.005	1
3611	0.007	2	8822	0.062	1
3636	0.006	1	8911	0.006	3
5811	0.010	1	9714	0.004	4

Table C-5. Sample 2: Beryllium (0.050 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5	0.048	1	5923	0.060	1
1113	0.050	5	5923	0.050	2
2311	0.081	1	6112	0.044	1
2726	0.530	1	7424	0.050	1
3126	0.018	1	7526	0.049	1
3611	0.080	2	8822	0.434	1
3636	0.030	1	8911	0.050	3
5811	0.075	1	9714	0.051	4

Table C-6. Sample 3: Beryllium (0.100 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5	0.094	1	5923	0.140	1
1113	0.250	5	5923	0.100	2
2311	0.150	1	6112	0.097	1
2726	1.150	1	7424	0.100	1
3126	0.046	1	7526	0.075	1
3611	0.160	2	8822	1.140	1
3636	0.078	1	8911	0.095	3
5811	0.150	1	9714	0.119	4

Table C-7. Sample 1: Barium (0.50 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5	0.49	1	4611	0.60	1
1113	0.38	5	5116	0.66	3
2311	0.55	1	5811	0.00	2
2726	0.50	1	5923	0.50	1
3126	0.30	1	6112	0.50	1
3226	0.65	1	7424	0.50	1
3324	0.52	1	8112	0.58	1
3611	0.30	6	8822	0.60	1
3636	0.88	1	9714	0.28	4
4211	0.41	2			

Table C-8. Sample 2: Barium (1.000 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5	0.98	1	4611	1.00	1
1113	0.74	5	5116	1.53	3
2311	1.12	1	5811	0.16	2
2726	1.00	1	5923	1.00	1
3126	0.72	1	6112	0.95	1
3224	1.20	1	7424	1.00	1
3326	1.04	1	8112	1.13	1
3611	0.92	6	8822	0.88	1
3636	1.63	1	9714	1.13	4
4211	0.95	2			

Table C-9. Sample 3: Barium (5.000 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
5	4.90	1	4611	5.00	1
1113	3.50	5	5116	5.56	3
2311	5.22	1	5811	1.40	2
2726	5.25	1	5923	5.40	1
3126	4.80	1	6112	5.00	1
3226	5.15	1	7424	5.00	1
3326	4.79	1	8112	5.18	1
3636	6.02	1	8822	5.18	1
4211	4.80	2			

APPENDIX D

GLOSSARY OF STATISTICAL TERMS

A glossary of statistical terms defined as they are used in this report is presented to ensure uniformity of understanding.

Arithmetic mean — The sum of the sample results divided by the number of results in the sample. Let X_i ($i = 1, 2, \ldots, n$) denote the i^{th} results in a sample of n results. The arithmetic mean denoted $\overline{X}$ is given by $\overline{X} = \sum_{i=1}^{n} \frac{X_i}{n}$.

Median — Halfway point in the results when they have been arranged in order of magnitude (the middle result of an odd number of results, or the average of the middle two for an even number).

Accuracy — The correctness of a measurement, or the degree of correspondence between the results and the true value (actual amount added).

Measures of accuracy — Measures that relate to the difference between the mean of the results and the true value when the latter is known or assumed. The following measures apply:

Mean error — The average difference with regard to sign between the results and the true value. Equivalently, the difference between the mean of the results and the true value (T. V.).

$$\text{Mean error} = \overline{X} - \text{T. V.}$$

Relative error — The absolute value of the mean error expressed as a percentage of the true value.

$$\text{Relative error} = \frac{|\overline{X} - \text{T. V.}|}{\text{T. V.}} \times 100$$

Precision — The reproducibility of sample results or the degree of agreement among the results.

Measures of precision

Measures of the variation among the sample results themselves, i.e., the spread or dispersion of the results without regard to the true value. The following measures apply.

Sample variance — Sum of squared deviations of the sample results from their mean divided by one less than the number of results in the sample. The sample variance denoted s^2 is given by

$$s^2 = \frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n - 1}$$

where n is the number of results.

Sample standard deviation — Square root of the sample variance.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n - 1}}$$

Relative standard deviation (coefficient of variation) — Sample standard deviation expressed as a percentage of the mean.

$$\text{Rel. Std. Dev.} = \frac{s}{\bar{X}} \times 100$$

Range — The difference between the largest and smallest results in the sample.

Confidence limits — Limits within which the true mean, μ, of the population (the theoretically infinite number of possible replications of the analysis) will lie with probability equal to $1 - \alpha$, where α is the probability that the limits do not contain the true mean. The upper and lower $1 - \alpha$ confidence limits are given by

$$\text{Confidence limits} = \bar{X} \pm t_{\alpha/2} s/\sqrt{n}$$

where $\overline{X}$ and s are the sample mean and standard deviation, $t_{\alpha/2}$ is the upper $\alpha/2$ point of "Student's" t-distribution, and n is the number of results in the sample used to compute $\overline{X}$.

Tolerance limits — Limits within which one can state with probability γ that at least a proportion P of the entire population will lie. The upper and lower tolerance limits are given by

$$\text{Tolerance limits} = \overline{X} \pm Ks,$$

where K is the factor for two-sided tolerance limits for normal populations.[1] The value of K depends upon the chosen values of γ and P.

REFERENCES

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APPENDIX E

TESTS FOR NORMALITY AND REJECTION OF OUTLIERS

Test for normality

The Kolmogorov-Smirnov goodness-of-fit test was used to determine whether the observations reported could reasonably be thought to have come from a normal distribution.[1]

Briefly, the test involves computing the observed cumulative frequency distribution (the percent of values less than or equal to each value in the distribution) and comparing it with the theoretical normal cumulative frequency distribution. The point at which the two distributions, theoretical and observed, show greatest divergence is determined. Reference of the value of the divergence to a table of critical values for the Kolmogorov-Smirnov goodness-of-fit test indicates whether such a large divergence is likely on the basis of chance. If such a large divergence is not likely, the distribution is designated as nonnormal; otherwise the distribution is designated as normal.

Tests for rejection of outliers

1. If the distribution is designated as nonnormal, the suspected outlier (the farthest value from the mean) is rejected only if the distance between it and the mean is greater than three standard deviations; otherwise the suspected outlier is accepted.

2. If the distribution is designated as normal and the sample size is less than or equal to 30, the suspected outlier, the farthest value from the mean, is tested for rejection by a method developed by Dixon.[2] Briefly, this test involves computing a ratio that compares the distance of the suspected value being tested from its neighbors with the range of all, or most all, of the observations (depending on the total number of suspected values in the sample). Reference of the ratio to a table of critical values for test ratios for gross errors indicates whether such a large ratio is likely on the basis of chance. If the ratio is greater than or equal to the critical value, the probability that the suspected outlier is from the sample distribution is small; hence, the outlier is rejected. If the ratio is less than the critical value, the suspected outlier probably came from the sample distribution; hence, the suspected outlier is accepted.

3. If the distribution is designated as normal, and the sample size is greater than 30, the suspected outlier is tested for rejection by a method developed by Santner.[3] This method employs the statistic, $\frac{\overline{X} - X_o}{s}$, where $\overline{X}$ is the sample mean, X_o is the suspected outlier (the

farthest value from the mean) and s is the sample standard deviation. This statistic is compared with a table of critical values to determine whether its value is larger than would be expected on the basis of chance. If the statistic is greater than or equal to the critical value, the suspected outlier is rejected; otherwise, the suspected outlier is accepted.

Application of tests for normality and for rejection of outliers to ARS studies

The test for normality and the subsequent test for rejection of outliers are applied to the observed data in two ways: first, to each method for a given substance at a given concentration; then to a given substance at a given concentration regardless of method. In either case, it is first necessary to determine whether the original distribution is normal or nonnormal. If the original distribution is designated as nonnormal, method 1 is used to test for rejection of the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests for normality or rejection of outliers are made, and the distribution is designated as nonnormal. On the other hand, if the suspected outlier is rejected, the new distribution, which excludes the rejected observation, is then tested for normality. If the new distribution is nonnormal, the next suspected outlier is tested for rejection by method 1. This cycle of testing for normality and testing for rejection of outliers continues until a suspected value is not rejected or the test for normality designates the distribution as normal. If the distribution is designated as normal, subsequent tests for rejection of outliers made by method 2 or 3 are the same as if the original distribution had been normal. This case is discussed next.

If the original distribution is designated as normal or a new distribution that was originally nonnormal is designated as normal after the rejection of one or more outliers, and if the number of observations is not greater than 30, then method 2 is used to test for rejection the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution is tested for rejection, and so on until the suspected value of a new distribution is not rejected; when this occurs, no further tests are made, and the final distribution is designated as normal. On the other hand, if the number of observations in the original distribution is greater than 30, method 3 is used to test the suspected outlier for rejection. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, than the suspected outlier farthest from the mean of the new distribution, which excludes the rejected value, is tested for rejection. Testing for outliers continues by this method until a suspected outlier is not rejected or the number of

observations is no longer greater than 30, in which case, method 2 is used for testing for rejection of any remaining suspected outliers.

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APPENDIX F

COMPARISON OF METHODS FOR STATISTICALLY SIGNIFICANT DIFFERENCES IN PRECISION AND ACCURACY

The methods are compared in two ways with respect to precision and accuracy. In the first case, two methods are compared at a given concentration with respect to precision and to accuracy. The unknown variances, σ_1^2 and σ_2^2 (estimated by the sample variances, s_1^2 and s_2^2), of the two methods are first compared by the F-test[1] to determine whether there is a significant difference in the precision of the two methods. The unknown means, μ_1 and μ_2 (estimated by the sample means, $\bar{X}_1$ and $\bar{X}_2$), of the two methods are then compared by the t-test[2] to determine whether there is a significant difference in the accuracy of the two methods. The t-test employed is based on the result of the F-test. These two tests of hypotheses will produce one of the following results.

Outcome 1: $\sigma_1^2 = \sigma_2^2$, $\mu_1 = \mu_2$

Outcome 2: $\sigma_1^2 = \sigma_2^2$, $\mu_1 \neq \mu_2$

Outcome 3: $\sigma_1^2 \neq \sigma_2^2$, $\mu_1 = \mu_2$

Outcome 4: $\sigma_1^2 \neq \sigma_2^2$, $\mu_1 \neq \mu_2$

In outcome 1, we conclude that the sample results do not indicate that a significant difference in either precision or accuracy exists between the two methods.

In outcome 2, we conclude that there is no indication of a significant difference in precision between the two methods, but there is a significant difference in the accuracy of the two methods; specifically, the method whose sample mean is closer to the true value is deemed the more accurate. In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the two methods, but the method with the smaller sample variance is the more precise.

In outcome 4, we conclude that there is a significant difference in the precision and in the accuracy of the two methods. The method with the smaller sample variance is the more precise, and the method whose sample mean is closer to the true value is the more accurate.

In the second case, more than two methods are compared at a given level of concentration with respect to precision and accuracy. Bartlett's

Test[3] is used first to test the hypothesis of equality of the unknown variances, σ_i^2, of the methods in order to compare the precision of the methods. If we conclude that the precision is the same, the Analysis of Variance[4] is then used to test whether a significant difference exists among the means, μ_i, in order to compare the accuracy of the methods. If there is a significant difference among the means. Duncan's Multiple Range Test[5, 6] is used to determine which method means differ significantly. If the precision is not the same, then the Kruskal-Wallis One-way Analysis of Variance by Ranks[7] is used to determine whether a significant difference exists among the means in order to compare the accuracy of the methods.

Once again, there are basically four possible outcomes for the above tests of hypotheses.

Outcome 1: all σ_i^2 are equal, all μ_i are equal

Outcome 2: all σ_i^2 are equal, not all μ_i are equal

Outcome 3: not all σ_i^2 are equal, all μ_i are equal

Outcome 4: not all σ_i^2 are equal, not all μ_i are equal

In outcome 1, we conclude that the sample results do not indicate a significant difference in either the precision or the accuracy of the methods.

In outcome 2, we conclude that there is no indication of a significant difference in the precision of the methods; however, at least one method does differ significantly from the rest with respect to accuracy, and Duncan's Multiple Range Test indicates which methods differ. For example, in comparing four methods, we might conclude $\mu_1 = \mu_2$ and $\mu_3 = \mu_4$, but μ_1 and μ_2 differ significantly from μ_3 and μ_4; or we might conclude that $\mu_1 = \mu_2 = \mu_3$, but μ_4 differs significantly from μ_1, μ_2, and μ_3.

In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the methods, but at least one method differs significantly from the rest with respect to precision.

In outcome 4, we conclude that the methods differ significantly with respect to both precision and accuracy.

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APPENDIX G

ANALYTICAL REFERENCE SERVICE MEMBERSHIP

STATE AGENCIES

Alabama State Department of Public Health, Montgomery
Alabama Water Improvement Commission, Montgomery
Arizona State Department of Health, Phoenix
Arkansas Pollution Control Commission, Little Rock
Arkansas State Department of Health, Little Rock
California Department of Water Resources, Sacramento
California State Department of Public Health, Los Angeles
California State Department of Public Health, Air and Industrial Hygiene Laboratory, Berkeley
California State Department of Public Health, Sanitation and Radiation Laboratory, Berkeley
Colorado Department of Public Health, Denver
Connecticut State Department of Health, Hartford
Delaware Water and Air Resources Commission, Dover
District of Columbia Department of Public Health, Washington, D. C.
Florida Department of Agriculture, Tallahassee
Florida State Board of Health, Jacksonville
Florida State Board of Health, Pensacola
Florida State Board of Health, Winter Haven
Hawaii State Department of Health, Laboratories Branch, Honolulu
Hawaii State Department of Health, Occupational and Radiological Health Section, Honolulu
Idaho Department of Health, Boise
Illinois Department of Public Health, Springfield
Illinois State Water Survey, Champaign
Illinois State Water Survey, Peoria
Indiana State Board of Health, Indianapolis
Iowa State Hygienic Laboratory, Des Moines
Iowa State Hygienic Laboratory, Iowa City
Kentucky State Department of Health, Division of Laboratory Services, Frankfort
Kentucky State Department of Health, Radiological Health Program, Frankfort
Lawrence Experiment Station, Massachusetts
Louisiana State Department of Health, New Orleans
Los Angeles County Flood Control District, California
Maryland State Department of Health, Bureau of Environmental Chemistry, Baltimore
Maryland State Department of Health, Bureau of Laboratories, Baltimore
Maryland State Department of Water Resources, Annapolis

Massachusetts Department of Public Health, Amherst
Massachusetts Department of Public Health, Boston
Michigan Department of Conservation, Lansing
Michigan Department of Public Health, Lansing
Minnesota Department of Agriculture, St. Paul
Minnesota Department of Health, Minneapolis
Missouri Department of Health, Jefferson City
Montana Bureau of Mines and Geology, Butte
Montana Health Department, Helena
Nebraska State Department of Health, Lincoln
Nevada State Department of Health, Reno
Nevada State Department of Health and Welfare, Las Vegas
New Hampshire State Department of Health, Concord
New Hampshire Water Supply and Pollution Control Commission, Concord
New Jersey State Department of Health, Trenton
New Mexico Department of Public Health, Santa Fe
New York State Conservation Department, Avon
New York State Conservation Department, Ronkonkoma
New York State Department of Health, Division of Air Resources, Albany
New York State Department of Health, Division of Laboratories and Research, Albany
New York State Department of Health, Syracuse
New York State Department of Labor, New York City
North Carolina Department of Water and Air Resources, Raleigh
North Dakota State Department of Health, Bismarck
North Jersey District Water Supply Commission, Wanaque
Ohio Department of Agriculture, Reynoldsburg
Ohio State Department of Health, Columbus
Oklahoma State Health Department, Oklahoma City
Oregon State Board of Health, Portland
Pennsylvania Department of Agriculture, Harrisburg
Pennsylvania Department of Health, Division of Air Pollution Control, Harrisburg
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Puerto Rico Institute of Health Laboratories, Hato Rey
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South Carolina Pollution Control Authority, Columbia
South Dakota Department of Health, Pierre
Tennessee Department of Public Health, Nashville
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Texas State Department of Health, Austin
Utah State Department of Health, Salt Lake City
Vermont State Department of Health, Barre
Vermont State Department of Health, Burlington

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Virginia State Department of Health, Bureau of Laboratories, Richmond
Virginia State Water Control Board, Richmond
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Albuquerque Department of Environmental Health, Food and Institutional Division, New Mexico
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City of Cincinnati, Division of Water Pollution Control, Ohio
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City of Niagara Falls, Division of Water Laboratories, New York
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DHEW, PHS, Northeast Marine Health Sciences Laboratory, Narragansett, Rhode Island
DHEW, PHS, Northeastern Radiological Health Laboratory, Winchester, Massachusetts
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Tennessee Valley Authority, Muscle Shoals, Alabama
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USDI, FWPCA, Analytical Quality Control, Cincinnati, Ohio
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Hach Chemical Company, Ames, Iowa
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Hydro Research Laboratories, Pontiac, Michigan
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INFILCO, General American Transportation Corporation, Tucson, Arizona
Ionac Chemical Company, Birmingham, New Jersey
Ionics, Incorporated, Watertown, Massachusetts
Isotopes - A Teledyne Company, Sandusky, Ohio
Isotopes, Incorporated, Palo Alto, California
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Kem-Tech Laboratories, Incorporated, Baton Rouge, Louisiana
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W. R. Grace and Company, Lake Zurich, Illinois
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Water Pollution Control Federation, Washington, D. C.
Water Service Laboratories, Incorporated, New York, New York
Xerox Corporation, Webster, New York
York Research Corporation, Stamford, Connecticut